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**SULFUR K-EDGE XANES AND TR-XRD STUDIES OF Pt-BaO/Al<sub>2</sub>O<sub>3</sub> LEAN NO<sub>x</sub> TRAP CATALYSTS: EFFECTS OF BARIUM LOADING ON DESULFATION**

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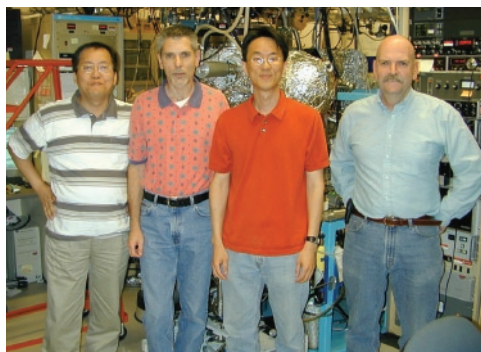
*Sulfur K-edge x-ray absorption near-edge spectroscopy (XANES) and in situ time-resolved x-ray diffraction (TR-XRD) are used to show that the removal of sulfur (in the form of BaSO<sub>4</sub>) from Pt-BaO(x)/Al<sub>2</sub>O<sub>3</sub> (x = wt% BaO) catalysts is strongly dependant on barium loading. Sulfated Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub>, consisting predominantly of monolayer BaO/BaCO<sub>3</sub> species, displays more facile desulfation by H<sub>2</sub> at lower temperatures than sulfated Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub>, a material containing primarily particulate BaO/BaCO<sub>3</sub> species. This suggests that the initial morphology differences between the two samples play a crucial role in determining the extent of desulfation and the temperature at which it occurs, a result that may be important in developing more sulfur-resistant LNT catalyst systems.*

Internal combustion engines operating under lean-burn conditions, such as diesel engines, exhibit high fuel efficiency. Removal of harmful NO<sub>x</sub> emissions from the exhaust in the presence of excess oxygen, however, presents a great challenge to the catalysis community because traditional three-way catalysts are ineffective under these conditions. Among the approaches being considered, urea and hydrocarbon selective catalytic reduction (SCR), and lean-NO<sub>x</sub> traps (LNTs, aka NO<sub>x</sub> storage/reduction (NSR) catalysts or NO<sub>x</sub> adsorb-ers) are promising technologies. In LNT technology, an active oxide (alkali and/or alkaline earth) material takes up NO<sub>x</sub> under lean engine operation conditions and stores them as nitrates. In a brief rich cycle, these nitrates are released from the active oxide catalyst component, and reduced to N<sub>2</sub> on the precious metal component of the catalyst.

Because even low concentrations of SO<sub>2</sub> in the emission gradually reduces the ability of the active

phase to store NO<sub>x</sub>, the resistance of the material to SO<sub>2</sub> poisoning remains a critical issue. Meanwhile, since we have shown that NO<sub>x</sub> adsorption/desorption chemistry is strongly dependent on the loading of barium, an important question concerns the variation of the desulfation chemistry as a function of barium content in the LNT formulation. As such, we performed a multi-spectroscopy study to understand desulfation processes on Pt-BaO/Al<sub>2</sub>O<sub>3</sub> LNT materials with varying barium loadings. In particular, we investigated the desulfation behavior of pre-sulfated Pt-BaO(8 or 20 wt%)/Al<sub>2</sub>O<sub>3</sub> catalysts using H<sub>2</sub> temperature programmed reaction (TPRx). These two BaO loadings were chosen because we have previously shown that the Ba-phase morphologies are significantly different; notably, BaO consists of a monolayer "coating" on the alumina surface in Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub>, while this monolayer phase coexists with a "particulate" or bulk-like BaO phase in the Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub> sample. Thus, we also followed the changes in catalyst morphology and sulfur oxidation states during desulfation processes using synchrotron time-resolved x-ray diffraction (TR-XRD) and sulfur K-edge x-ray absorption near-edge spectroscopy (XANES), which were performed on the NSLS beamlines X7B and X19A, respectively.

**Figure 1** shows the H<sub>2</sub> TPRx spectra of sulfated Pt-BaO(8)/Al<sub>2</sub>O<sub>3</sub> and Pt-BaO(20)/Al<sub>2</sub>O<sub>3</sub> samples, obtained by ramping the temperature of these samples in a H<sub>2</sub>/He flow while continually monitoring the product gases with a mass spectrometer. H<sub>2</sub>S is the primary product of the reaction between H<sub>2</sub> and sulfur species on the sample. H<sub>2</sub>S is formed at higher temperature for the sample with higher barium loading, implying that the type



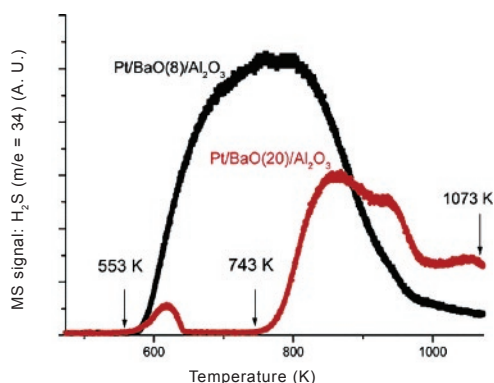
Authors (from left) Ja Hun Kwak, Janos Szanyi, Do Heui Kim, and Chuck Peden

of barium sulfate species formed upon uptake of  $\text{SO}_2$  is different depending on the loading of barium species – surface or ‘monolayer’ sulfates for Pt-BaO(8)/ $\text{Al}_2\text{O}_3$ , and ‘bulk’  $\text{BaSO}_4$  for the Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample. In addition, the amount of  $\text{H}_2\text{S}$  produced over Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  is two times larger than that of the sample with higher barium loadings, which suggests a more facile desulfation of ‘monolayer’  $\text{BaSO}_4$ .

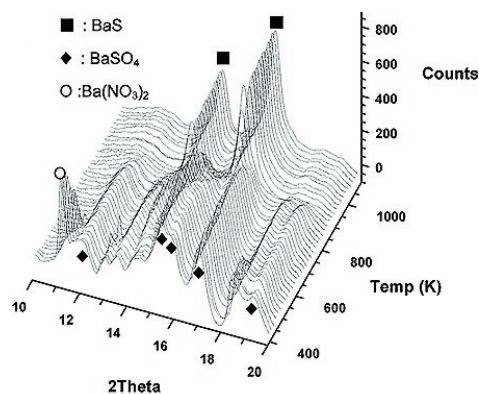
Sulfur K-edge XANES experiments were carried out to investigate changes in the oxidation states of sulfur as a function of  $\text{H}_2$  reduction temperature. We collected samples after  $\text{H}_2$  TPRx up to 553 K, 743 K and 1073 K (see arrows in **Figure 1**). After  $\text{H}_2$  TPRx up to 553 K for the sulfated Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  sample, the spectrum in **Figure 2(A)** contains a small peak at 2472 eV, which can be assigned to a sulfide-like ( $\text{S}^{2-}$ ) species, while the main sulfate ( $\text{SO}_4^{2-}$ ) peak is unchanged. After  $\text{H}_2$  TPRx up to 1073 K, the sulfate peak nearly disappears, while there is an increase in features from lower oxidation state sulfur species (sulfide-like

and sulfite-like ( $\text{SO}_3^{2-}$ )). The sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample shows qualitatively similar behavior as shown in **Figure 2(B)**. However, compared with the sample with lower barium loading, Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  contains a significantly larger amount of residual sulfur species of all types after  $\text{H}_2$  TPRx up to 1073 K, which is consistent with the  $\text{H}_2$  TPRx results.

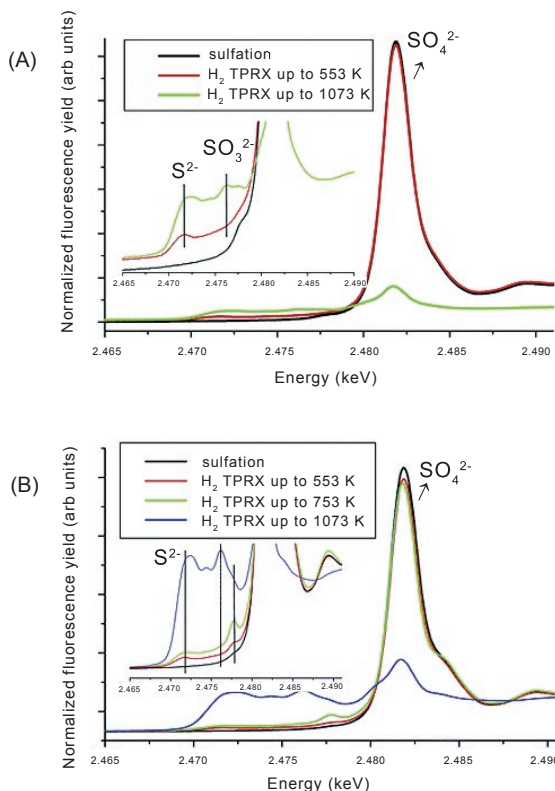
**Figure 3** shows a series of XRD patterns obtained during  $\text{H}_2$  TPRx for the sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample. The room temperature XRD contains peaks assigned to  $\text{BaSO}_4$ . Up to about 773 K, the  $\text{BaSO}_4$  phase is unchanged. However, above 773 K, diffraction peaks associated with BaS appear and continue to grow with increasing temperature, along with a corresponding drop in the intensities of the  $\text{BaSO}_4$  peaks. Compared with the Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample, Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  contains much smaller amounts of BaS, confirming that residual sulfur species were present at much lower concentrations for the lower barium loading sample.



**Figure 1.**  $\text{H}_2$  TPRx spectra for sulfated Pt-BaO(8)/ $\text{Al}_2\text{O}_3$  and Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  samples.



**Figure 3.** TR-XRD patterns collected during  $\text{H}_2$  TPRx from a sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  sample.



**Figure 2.** Sulfur K-edge XANES spectra of (A) sulfated Pt-BaO(8)/ $\text{Al}_2\text{O}_3$ , and (B) sulfated Pt-BaO(20)/ $\text{Al}_2\text{O}_3$  samples.